

High-temperature thermoluminescence of anion-deficient corundum and its connection with intrinsic defects and impurities

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Abstract. Anion-deficient corundum and TLD-500 detectors on their basis were studied for a possible correlation between the thermoluminescence (TL) yield in the high-temperature TL peak at 830 K and the transformation of intrinsic defects and contents of impurities. Only 40–60% of TLD-500 detectors were found to have 830 K TL peak. The efficiency of thermally stimulated direct conversion of F and F⁺ centers in the 800–930 K region depends on the presence of TL peak at 830 K. Obtained data point to the quenching role of the Ti impurity in the formation of the 830 K TL peak. Also, these data provide indirect evidence of association of the 830 K TL peak with Cr³⁺ ions.

1. Introduction

It was found in [1, 2, 3] that thermoluminescence (TL) response in TLD-500 detectors based on anion-deficient corundum (α -Al₂O_{3-δ}) is dose-proportional in the high-temperature peak at 830 K. In cases where continuous irradiation is used, such response is proportional to a dose up to 2 kGy. At pulsed nanosecond irradiation, it is proportional to a dose up to 6 MGy. In [3], the TL spectrum in the peak at 830 K was also studied to reveal, along with weak luminescence of F⁺ centers (anion vacancy with one electron) with $h\nu_{em}=3.4$ eV, intense luminescence with $h\nu_{em}=4.1$ eV whose nature is not known precisely. Similar luminescence was only observed earlier at $T \leq 300$ K and was caused by excitons localized at Ti-ions [4]. It is also known that the luminescence of F centers (anion vacancy with two electrons) at $T > 700$ K including the high-temperature peak was thermally quenched. One of the difficulties and still unresolved problems for anion-deficient corundum is also the fact that so far no correlations have been discovered between the impurity composition, concentration of active F⁺ and F centers, and the TL yield in the main dosimetric peak at 450 K. For above room temperatures, the research has precisely established only the relationship of the TL yield in the 570–600 K peak with chromium impurity [5]. It is caused mainly by the luminescence of Cr³⁺ ions and is therefore called "chromium" peak. The objective of this study is detection in α -Al₂O_{3-δ} of possible correlations of TL output in the high-temperature peak at 830 K with the transformation of intrinsic defects and contents of impurities.



2. Samples and experimental techniques

The objects of this study were samples of TLD-500 detectors on the basis of α - $\text{Al}_2\text{O}_3\cdot\delta$ single crystals, some of which were discovered to lack the 830 K TL peak. The impurity composition in the detectors studied was checked by the X-ray fluorescent method using an XRF-1800 spectrometer. The samples were irradiated on UELV-10-10S accelerator with 10 MeV electrons and with a bremsstrahlung by doses of 9 kGy and 300 Gy, respectively [3]. The TL curves were measured at a heating rate of $\beta=2$ K/s in a temperature range of $T=300\text{--}1100$ K. The TL signal was recorded by a FEU-142 photomultiplier at a reduced sensitivity to the thermal radiation of the heater, the temperature of which could reach 1200 K. The samples were annealed directly in the spectrophotometers over a temperature range of $T_a=300\text{--}1400$ K with 20 K steps at $\beta=2$ K/s. Upon achieving the required T_a , the samples were cooled to 300 K, and their optical absorption (OA) spectra and PL were measured in two parallel experiments by means of a Cary 60 and a Cary Eclipse spectrophotometer, respectively. The concentrations of F and F^+ centers (C_F and C_{F^+} , respectively) were determined from OA in the bands with $h\nu_{m1}=6.1$ eV and $h\nu_{m2}=4.8$ eV, respectively, using Smakula's formula. According to [6], oscillator strengths were taken to be equal to 1.3 for the F center and to 0.65 for the F^+ center.

The time-integrated spectra of pulsed cathodoluminescence (PCL) were measured using a LineSpecTM CCD Array Spectrometer over a range of 1.4–5.6 eV with a time gate length of 20 ms for 10 s under excitation with an electron beam from an Arina-02 accelerator ($E_e=130$ KeV, $\tau_p=10$ ns, $W=7$ mJ/(cm²·pulse)).

3. Results and discussion

A study of TL in fairly large batches of TLD-500 detectors revealed the 830 K TL peak in only ~40–60% of the detectors. In the others, the TL peak at 830 K was not observed even after their continuous irradiation with 2–9 kGy doses.

Figure 1a shows changes in C_F (curve 1) and C_{F^+} (curve 2) in the samples with the 830 K TL peak depending on T_a . In the annealing temperature range under study, antibatic changes in the $C_F(T_a)$ and $C_{F^+}(T_a)$ are observed in them over the entire region of the step annealing procedure. The concentration change of Al_i^+ centers (C_{Al} , curve 3) (interstitial aluminium ion in an octahedral position absorbing and excited at $h\nu_{\text{ex}}=4.1$ eV and luminescing at $h\nu_{\text{em1}}=3.8$ eV and $h\nu_{\text{em2}}=2.4$ eV [7]) demonstrates a similar behavior under annealing to that of the F centers, with a prominent minimum near the main peak. Figure 1a also shows a TL curve ($I_{\text{TL}}(T)$, curve 4) in which one can easily discern the main, chromium and high-temperature peaks at 450, 570 and 830 K, respectively. Especially noteworthy is a substantial change in the $C_F(T_a)$, $C_{F^+}(T_a)$ and $C_{\text{Al}}(T_a)$ in the range of 830–920 K, that is in the high-temperature part of the 830 K TL peak and immediately after it. What we observe here is effective thermally stimulated direct ($\text{F}\rightarrow\text{F}^+$) conversion of F and F^+ centers. However, comparison of the changes in the C_F and C_{F^+} shows that annealing in the range of 830–920 K causes only ~30% of transformed F centers convert into F^+ centers. A similar situation is observed for the reverse conversion ($\text{F}^+\rightarrow\text{F}$) of F^+ into F centers at temperatures above 950 K.

Similar evidence of changes in the $C_F(T_a)$ (curve 1) and $C_{F^+}(T_a)$ (curve 2) in a sample without a detectable 830 K TL peak is presented in figure 1b. If we compare it with the data for a sample with the 830 K TL peak, one can see that changes in the $C_F(T_a)$ and $C_{F^+}(T_a)$ are also observed in the region of 830–920 K, but with a very low efficiency. Nevertheless, as well as in the case of the sample with the 830 K peak, in this case only ~30% of the transformed F centers will be converted into F^+ centers. Note also a substantial increase in the F center concentrations at annealing temperatures above 950 K along with an insignificant decrease in the concentration of F^+ centers.

By way of summarizing the data on changes in the concentrations of F^+ and F centers in the irradiated detectors of both types considered, we can assume that it is F^+ and F centers that actively participate in the formation of the high-temperature peak at 830 K, at least of its high-temperature part.

We therefore then compared the TL curves ($I_{\text{TL}}(T)$) in the samples with about similar and essentially different concentrations of anion vacancies C_a defined as $C_a=C_F+C_{F^+}$. As may be seen from

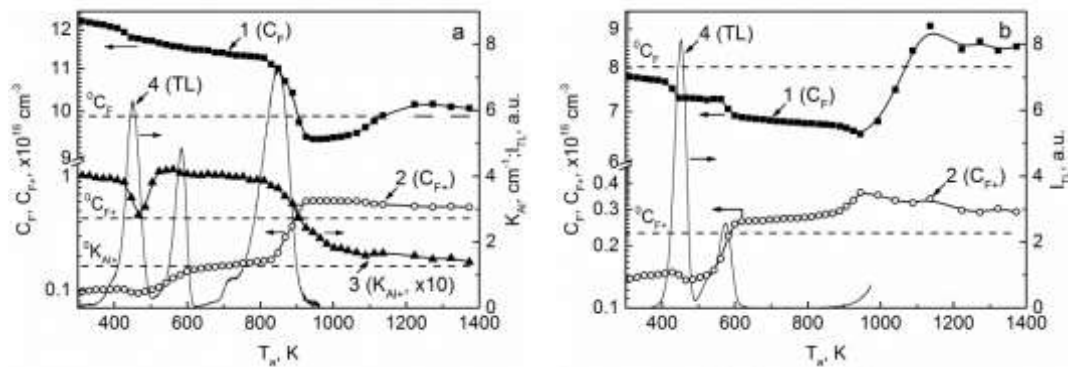


Figure 1. Changes in the concentrations of F (1), F⁺ (2) and Al_i⁺ (3) centers under step annealing and the TL curve (4) in samples irradiated with a dose of 9 kGy with the 830 K TL peak (part a) and without such a peak (part b).

figure 2 (curves 1 and 2), the two samples with about similar C_a ($C_{a1}=9.0 \cdot 10^{16} \text{ cm}^{-3}$ and $C_{a2}=9.3 \cdot 10^{16} \text{ cm}^{-3}$, respectively) have TL yields that are essentially different not only in the main peak but also in the high-temperature one. This pattern for the main peak has been known for a long time and, in our opinion, it is due to its nature. It is one of the varieties of Al_i⁺ center that is responsible for the main peak [8]. Thermal stimulation causes a restructuring of this center with the formation of F⁺ and F center-bound excitons, which, while relaxing, excite F⁺ and F centers.

To elicit the dependence of the TL yield at 830 K on C_a , half of the one of the samples with the 830 K peak was annealed in air at $T_a=1800 \text{ K}$ for 70 hours. After such thermal treatment, C_a decreased ~ 7 times ($1.3 \cdot 10^{16} \text{ cm}^{-3}$), the TL yield of the 830 K peak decreased ~ 2 times, and that of the 450 K peak decreased 15–20 times (figure 2, curve 3).

Thus, an analysis of these data reveals a certain relationship in $\alpha\text{-Al}_2\text{O}_{3-\delta}$ between the concentration of anionic vacancies and TL yield in the high-temperature peak, but it is not as significant as for the main peak. We may, therefore, assume that certain impurities or other intrinsic centers may be responsible for the TL response in the 830 K peak.

One of the sensitive methods for estimating the contribution of impurities to the relaxation process is cathodoluminescence. Figure 3 shows time-integrated PCL spectra for samples with the 830 K peak (curves 1 and 2, respectively), and samples without such a peak (curves 3 and 4, respectively). The spectra reveal the characteristic luminescence of F⁺, F and Al_i⁺ centers with $h\nu_{\text{em}}$ equal to 3.8, 3.0 and 2.4 eV, respectively, along with sufficiently intensive PCL of Cr³⁺, Ti³⁺ and Ti⁴⁺ centers with $h\nu_{\text{em}}$ equal to 1.79, 1.7, and 2.2, respectively. The interpretation of PCL for Ti³⁺ and Ti⁴⁺ centers is based on the data from [9].

The joint analysis of PCL and TL demonstrates that samples with the 830 K peak in which we did not detect PCL of Ti³⁺ centers with $h\nu_{\text{em}}=1.7 \text{ eV}$ display an intensive high-temperature peak at 830 K. In samples without the 830 K peak, such PCL is well detectable. Moreover, all spectra display a band with a maximum at 4.26 eV, which is most intensive in sample with the maximum luminescence of Ti³⁺ centers (curve 4).

In order to better understand the nature of the relaxation processes in $\alpha\text{-Al}_2\text{O}_{3-\delta}$, and in the region of the 830 K TL peak in particular, we studied in the next series of experiments changes in the PL response separately for Al_i⁺, Ti³⁺ and Cr³⁺ centers (I_{Al} , I_{Cr} and I_{Ti}) depending on T_a in the 300–1400 K range. The photoluminescence of Al_i⁺, Ti³⁺ and Cr³⁺ centers was excited at $h\nu_{\text{ex}}$, equal to 4.1, 2.5 and 2.2 eV, respectively, and the PL responses were read out at $h\nu_{\text{em}}$, equal to 2.4, 1.7 and 1.79 eV, respectively. This approach ensures a higher sensitivity than OA data in indentifying small changes in the concentrations of Al_i⁺, Ti³⁺ and Cr³⁺ centers in corundum under step-annealing, including in the region of the 830 K TL peak.

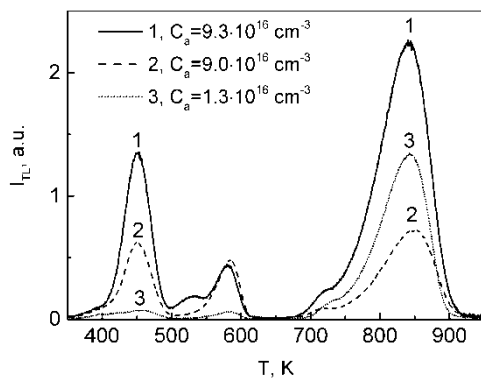


Figure 2. The TL curves of TLD-500 detectors irradiated with a dose of 300 Gy, with C_a : $9.3 \cdot 10^{16} \text{ cm}^{-3}$ (1), $9 \cdot 10^{16} \text{ cm}^{-3}$ (2), $1.3 \cdot 10^{16} \text{ cm}^{-3}$ (3).

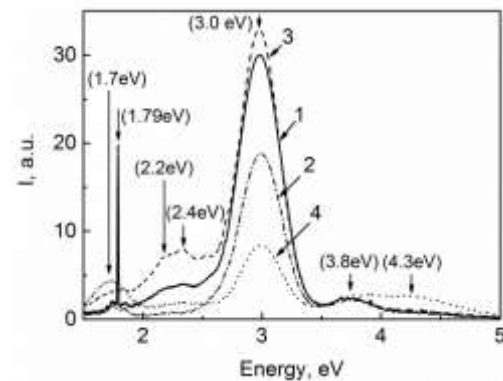


Figure 3. PCL spectra of samples with the 830 K peak (curves 1 and 2) and without such a peak (curves 3 and 4).

Figure 4 shows, for one of samples with the 830 K TL peak (part a) and for sample without such a peak (part b), the dependencies $I_{Al}(T_a)$, $I_{Cr}(T_a)$, $I_{Ti}(T_a)$ and $I_{TL}(T)$ (curves 1–4, respectively). In sample with the 830 K TL peak, the dependence $I_{Al}(T_a)$ is seen to vary in an extreme manner in the regions of the main and high-temperature peaks at 450 and 830 K and immediately after them, while $I_{Cr}(T_a)$ varies symbatically with $I_{TL}(T)$ in the chromium peak at 570 K and antibatically with $I_{TL}(T)$ in the 830 K peak. The extremely low PL response of the Ti^{3+} ions enables one just to identify its possible small increase in the region of the high-temperature peak.

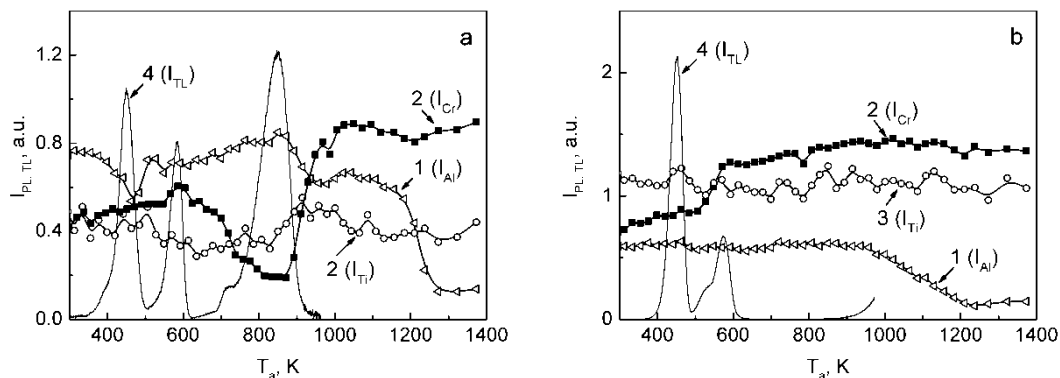


Figure 4. Changes in the intensity of Al_i^+ (1), Ti^{3+} (2) and Cr^{3+} (3) centers PL under step-annealing in samples irradiated with a dose of 9 kGy with the 830 K TL peak (part a) and without such a peak (part b). The figure also has TL curves (4) for samples with the 830 K TL peak (part a) and without such a peak (part b).

In the sample without the peak, the above changes in $I_{Al}(T_a)$, $I_{Cr}(T_a)$ и $I_{Ti}(T_a)$ were not detected in the region of $T_a=700\text{--}900 \text{ K}$ (Figure 4b). Nevertheless, step-annealing can help identify minor changes in $I_{Ti}(T_a)$ (curve 3) and $I_{Cr}(T_a)$ (curve 2) in the main and chromium peaks, respectively.

We may therefore state that in anion-deficient corundum samples with a high-temperature peak impurity and intrinsic Cr^{3+} , Ti^{3+} and Al_i^+ type centers may play a certain part in its formation.

X-ray fluorescent elemental analysis was therefore performed next for specially selected 8 samples of TLD-500 detectors having considerably differing TL yields at 830 K and containing, according to the PCL data, trace amounts of chromium and titanium impurities. The analytical data are summarized in Table 1, which also includes the values of C_a and TL yields in the region of the 830 K peak. Moreover, the data in Table 1 are arranged allowing for the TL yields of the samples in the region of

the 830 K peak. For the purpose of TL yield determination, the samples were irradiated with a bremsstrahlung dose of 300 Gy corresponding to the linear region of the dose dependence [3].

An analysis of the data presented in Table 1 shows that the concentration of the chromium impurity in the samples studied is rather small, varying insignificantly, no more than two times. The other impurities found, such as Mg, Si, Ca, Ti and Fe, differ in concentration ~ 3 –4 times as a minimum. The spread of the C_a values is ~ 8 times. It is important that neither the level of anion deficiency nor the changes in the concentration of each of the impurities found, except for the titanium, correlate with the TL yield in the 830 K peak. We may regard as the most significant result of the analysis the discovery of the quenching effect of the titanium impurity on the TL yield in the high-temperature peak at 830 K. As can be seen, the TL yield in the 830 K peak increases as the concentration of the titanium impurity decreases (C_{Ti}).

Table 1. The result of the X-ray fluorescent elemental analysis in specially selected TLD-500 detector samples

Sample number	Impurity concentration (10^{-4} wt.%)						$C_a \times 10^{-16}$ (cm^{-3})	TL output at 830 K
	Mg	Si	Ca	Ti	Cr	Fe		
1	77	<1	100	<7	78	17	7.8	167036
2	352	429	57	7	98	210	7.1	37532
3	<29	499	64	8	58	370	1.8	29041
4	29	<1	127	12	68	283	9.0	22744
5	190	54	45	13	61	92	8.5	11866
6	30	<1	78	17	73	89	9.3	7493
7	123	1	45	21	81	81	6.3	0
8	88	267	47	29	53	127	14.8	0

4. Conclusion

Thus, our data point to the quenching role of the titanium impurity in the formation of the 830 K high-temperature thermoluminescence peak. Also, the reported data provide indirect evidence of its association with Cr^{3+} ions. However, no reliable data have been obtained as yet on the nature of the UV glow with a maximum at 4.1 eV observed in the 830 K high-temperature peak. According to the data available to us, none of the types of active center in anion-deficient corundum, such as F^+ , F , Al_i^+ centers, are additionally excited at temperatures near 830 K. Nevertheless, what is possible for F^+ centers is radiative transition from higher excited states. The interaction between Cr^{3+} and Ti^{3+} ions that we observed can lead to the creation of a multiple component defect, including that with the participation of anion vacancies. Such a complex defect may get restructured in the relaxation process near 830 K, as is the case with Al_i^+ centers in the main dosimetric peak, and with the glow in the region of 4.1 eV.

Acknowledgements

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